Lawrence Livermore National Laboratory

# Predicting properties of plutonium metal and alloys within the dynamical mean field theory

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Computing Grand Challenge Symposium


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# Outline

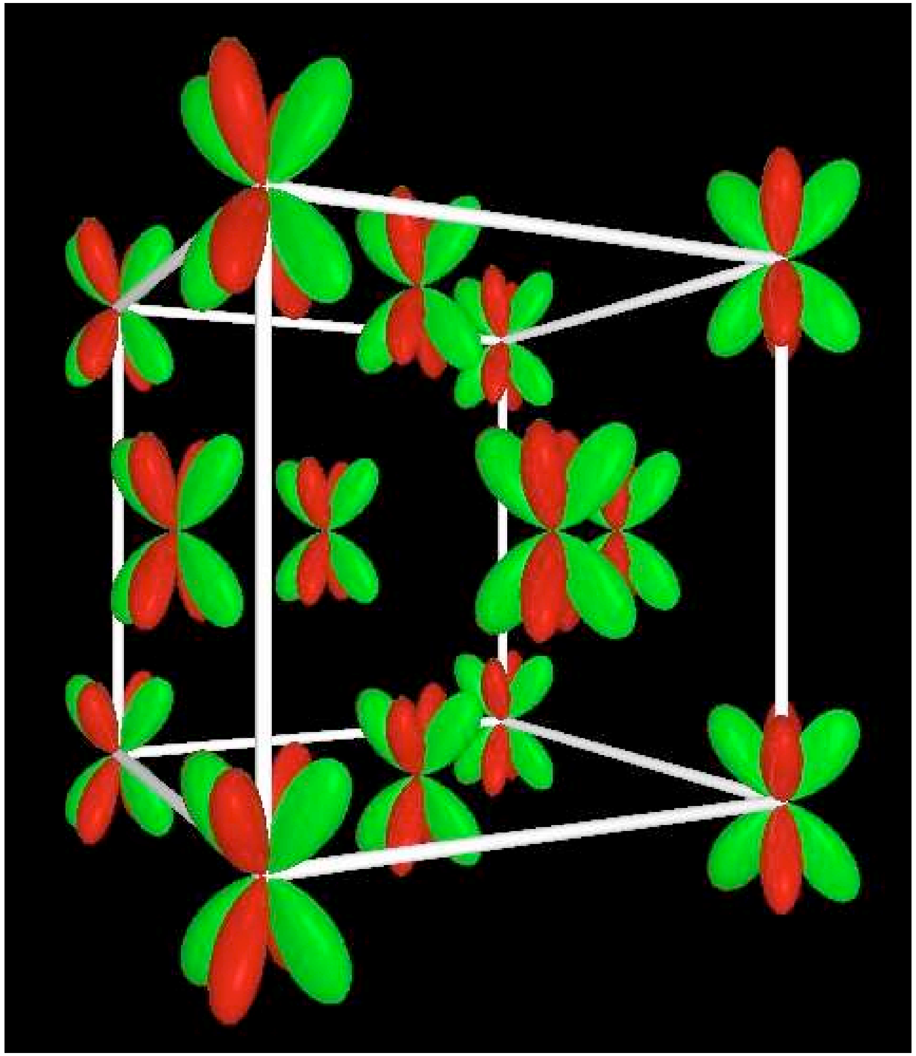
- Computational and scientific goals
- Methodology

$\longrightarrow$ Density functional theory (DFT)

$\longrightarrow$ Dynamical mean-field theory (DMFT)

$\longrightarrow$ Continuous time QMC approach (CTQMC)

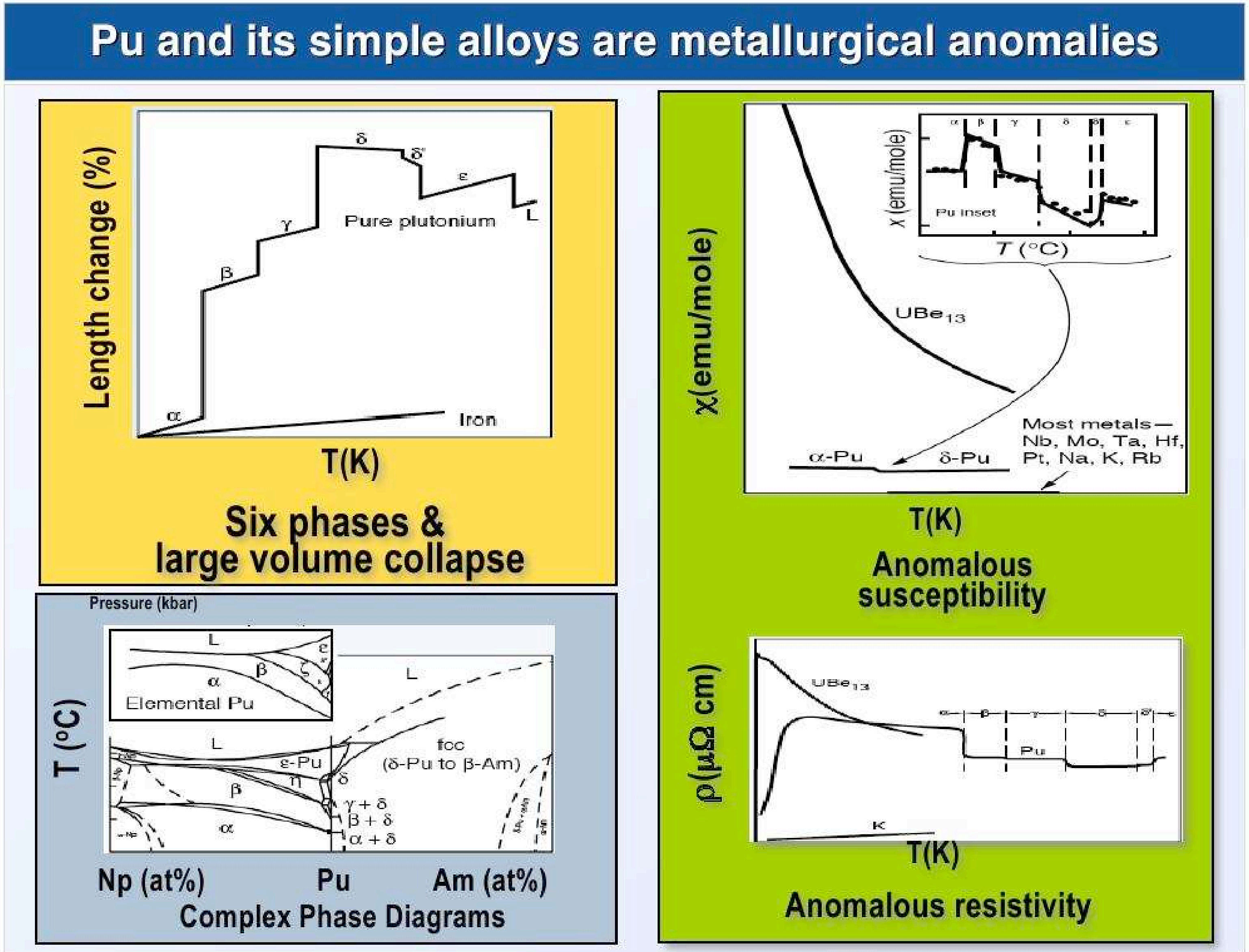
- DFT+DMFT computed properties of $\delta$ Pu
- Future work
- Conclusion



A schematic of $f_{xyz}$ orbitals in $\delta$ Pu

# Anomalous Properties of Pu

- Scientific objectives
  - → Absence of magnetism
  - → Volume collapse
  - → Role of alloying
- Electronic properties
  - → Spectra
  - → Heat capacity
  - → Magnetic susceptibility
  - → Fermi surface
  - → Resistivity




DMFT is positioned to meet this challenge

# General Methods

- Density functional theory (DFT) $\Rightarrow \Gamma[\rho]$

$\longrightarrow$ Realistic systems

$\longrightarrow$ Ground state properties

- Dynamical mean-field theory (DMFT) $\Rightarrow \Gamma[G]$

$\longrightarrow$ Model Hamiltonians

$\longrightarrow$ Captures physics of Mott transition

$\longrightarrow$ Ground/excited state properties

Merge approaches $\Rightarrow$ DFT+DMFT $\Rightarrow \Gamma[\rho, G]$

# DFT+DMFT for Pu

- DMFT too expensive to apply to all electrons

$\longrightarrow$ Even for Blue Gene!

- Only apply DMFT to most correlated electrons

$\longrightarrow$ $f$-electrons in Pu.

$\longrightarrow$ Apply DFT to the remaining electrons.

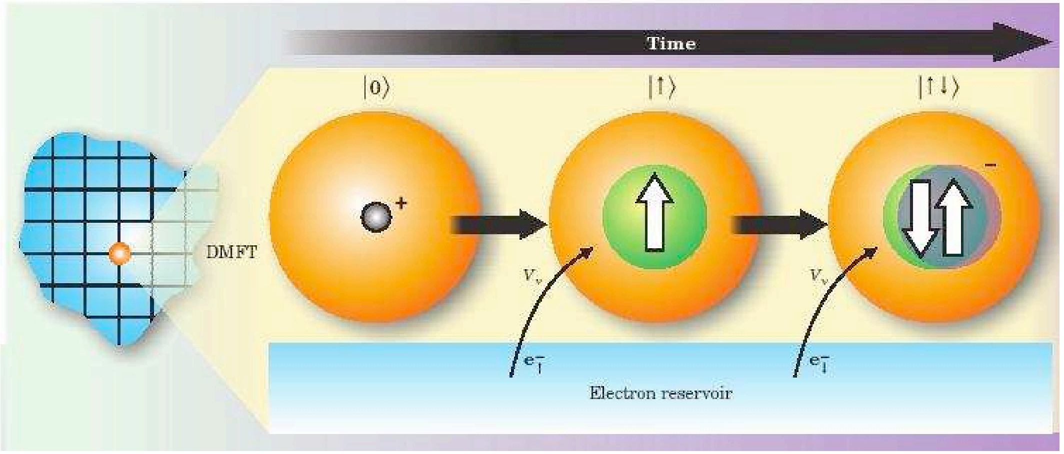
- Double-counting problem

$\longrightarrow$ Implication: number of $f$-electrons not accurately predicted.

$\longrightarrow$ Comparison with experiment must determine $f$-electron count

Nearly first-principles approach to strongly correlated materials

# DMFT: what is it?




$$H_{AIM} = \sum_{\sigma} \epsilon_{imp} c_{\sigma}^{+} c_{\sigma} + U c_{\uparrow}^{+} c_{\uparrow} c_{\downarrow}^{+} c_{\downarrow} + \sum_{k\sigma} V_k (a_{k\sigma}^{+} c_{\sigma} + c_{\sigma}^{+} a_{k\sigma}) + \sum_{k\sigma} \alpha_k a_k^{+} a_k$$

- *DMFT maps lattice many-body problem to Anderson impurity model (AIM).*
- AIM has 1 site of lattice embedded in bath of fictitious electrons which mimic removed lattice sites.
- Characteristics of fictitious electrons determined by DMFT self-consistency condition.
- AIM may be solved accurately using computation.

# Solving Anderson impurity model

- Quantum Monte-Carlo may be used to exactly solve AIM

$\longrightarrow$ Computational cost increases as temperature decreases

- Traditional Hirsch-Fye QMC method has limitations

$\longrightarrow$ Difficult to reach ambient temperatures

$\longrightarrow$ Cannot exactly treat on-site exchange

- Continuous time QMC (CTQMC) does not have these limitations

$\longrightarrow$ CTQMC stochastically sums the Feynman diagrams of the AIM.

$\longrightarrow$ CTQMC may be applied starting from the band limit or the atomic limit

Computation can provide the exact solution to the AIM!

# CTQMC: band limit vs. atomic limit

$$U = 0 \text{ vs. } V_k = 0$$

- Is Pu closer to atomic limit or band limit?
- Will one technique have convergence problems?
- Atomic limit performs significantly better.

$\longrightarrow$ Much better statistics per unit time.

- Why???

$\longrightarrow$ Obvious how to truncate basis in atomic limit.

$\longrightarrow$ Pu is actually closer to atomic-limit than band limit.

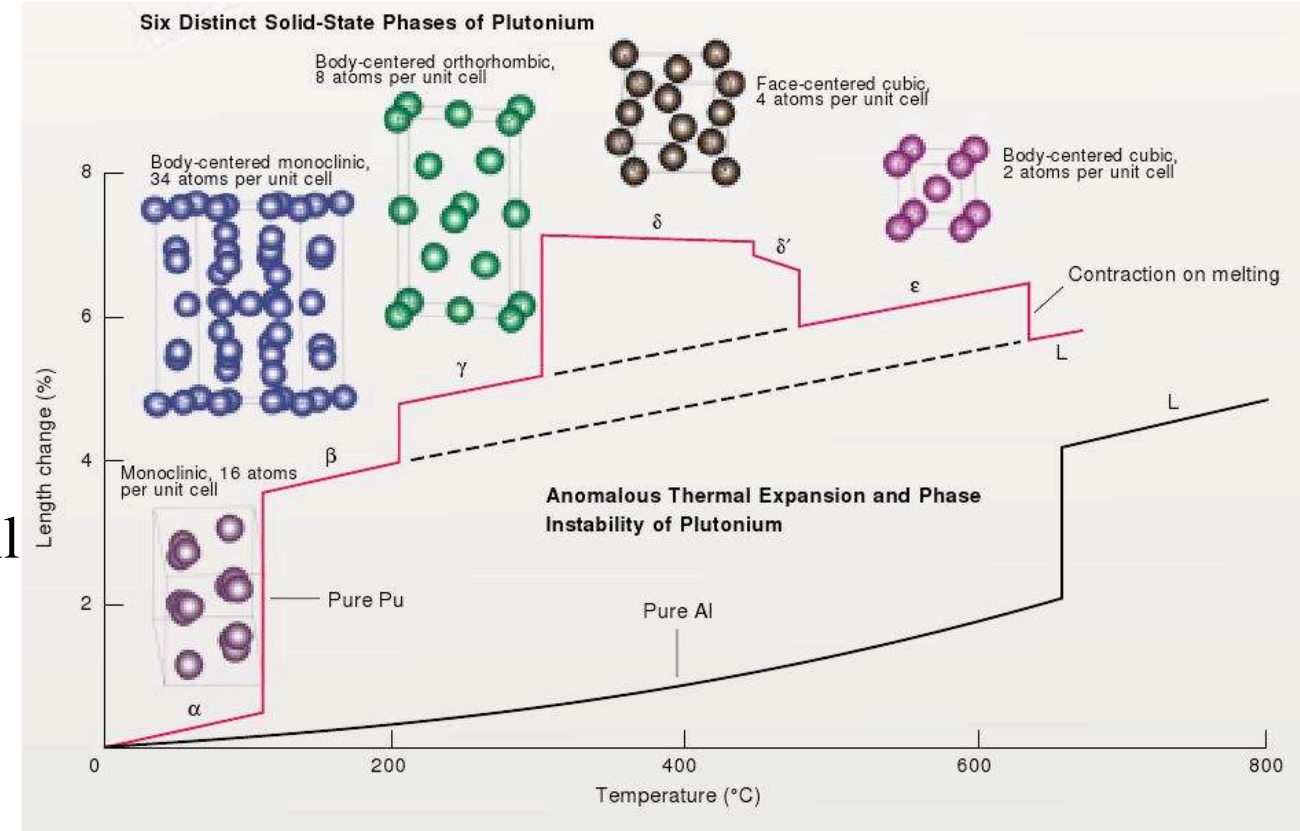
**CTQMC atomic limit is preferential for Pu**

# Computational Objectives

- Approximation-free DMFT
- Ambient temperatures and below
- Non-trivial structures

$\longrightarrow$ More than one atom per unit cell

- Measure various observables



# Computational Requirements

- QMC is rate limiting step of DFT+DMFT

$\longrightarrow$ Parallelizes nearly perfectly

$\longrightarrow$ More time $\Rightarrow$ more progress

- Average run $\approx$ 20k CPU-hours

$\longrightarrow$ 1 atom/cell

$\longrightarrow$ scales linearly with # of atoms

$\longrightarrow$ $\approx$ 40k CPU-hours for $T = 240K$

- Self-consistency in density

$\longrightarrow$ factor of 10 increase?

Atlas

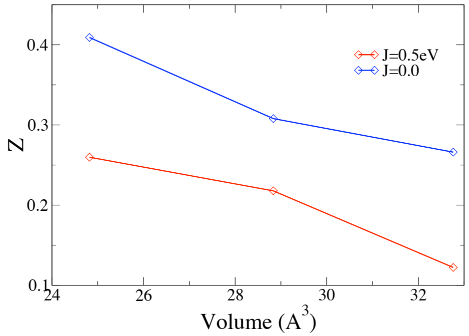
# Results for δ Pu

- Performed first approximation-free DMFT

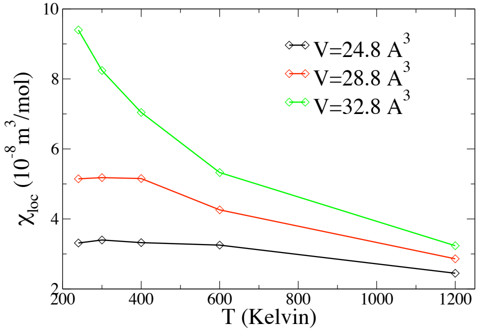
→ Including full exchange interaction

- Calculated various properties

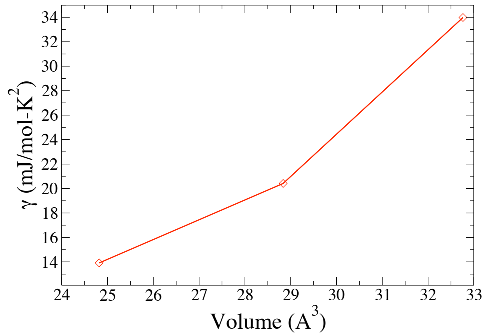
→ Quasiparticle weight



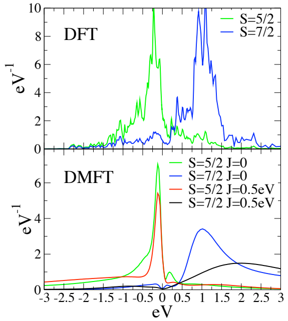

→ Magnetic susceptibility




→ Heat capacity




→ Spectra



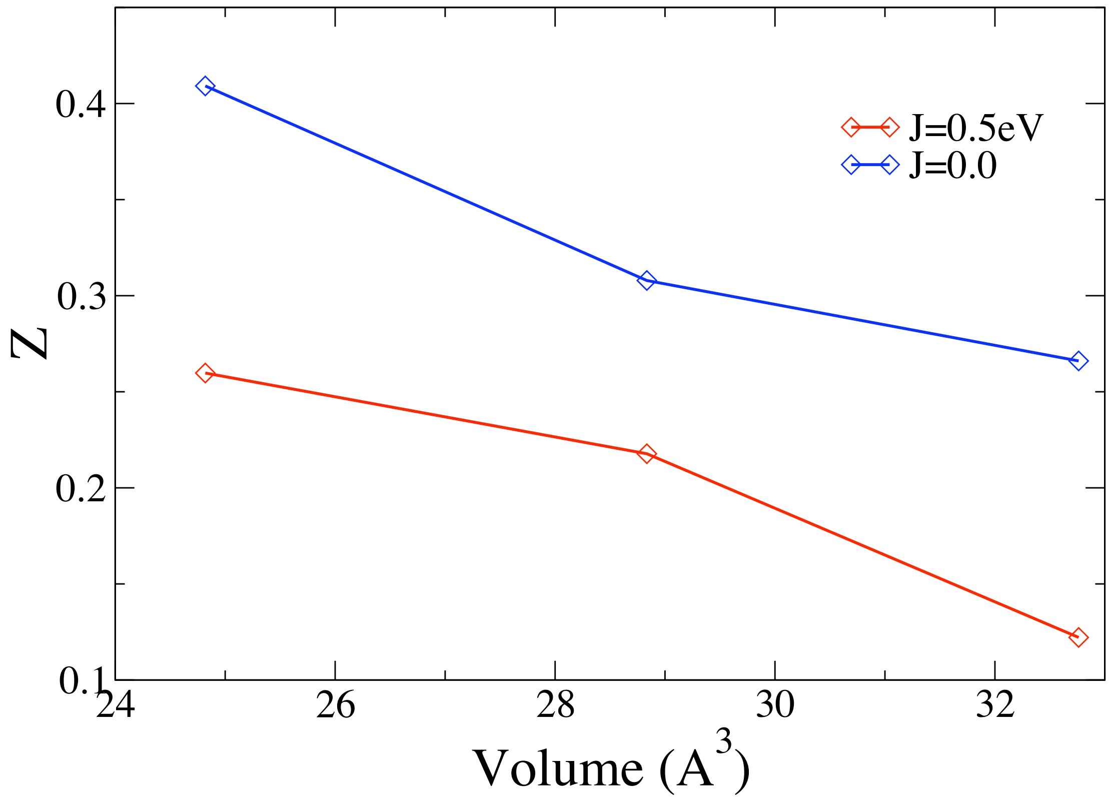
# Quasiparticle Weight $Z = \frac{1}{m^*}$

- Z is inverse of effective mass

$\longrightarrow$ Z=1 $\Rightarrow$ no correlations

$\longrightarrow$ Z=0 $\Rightarrow$ electrons localize

- Pu is closer to atomic limit
- Electrons become heavier as volume increases
- Including exchange substantially increases correlations.




**Pu is strongly correlated**

# Linear Coefficient of Heat Capacity

- Low temperature heat capacity sensitive to correlations.
- Strongly depends on volume.
- Experiments find $35 - 65 \frac{mJ}{molK^2}$

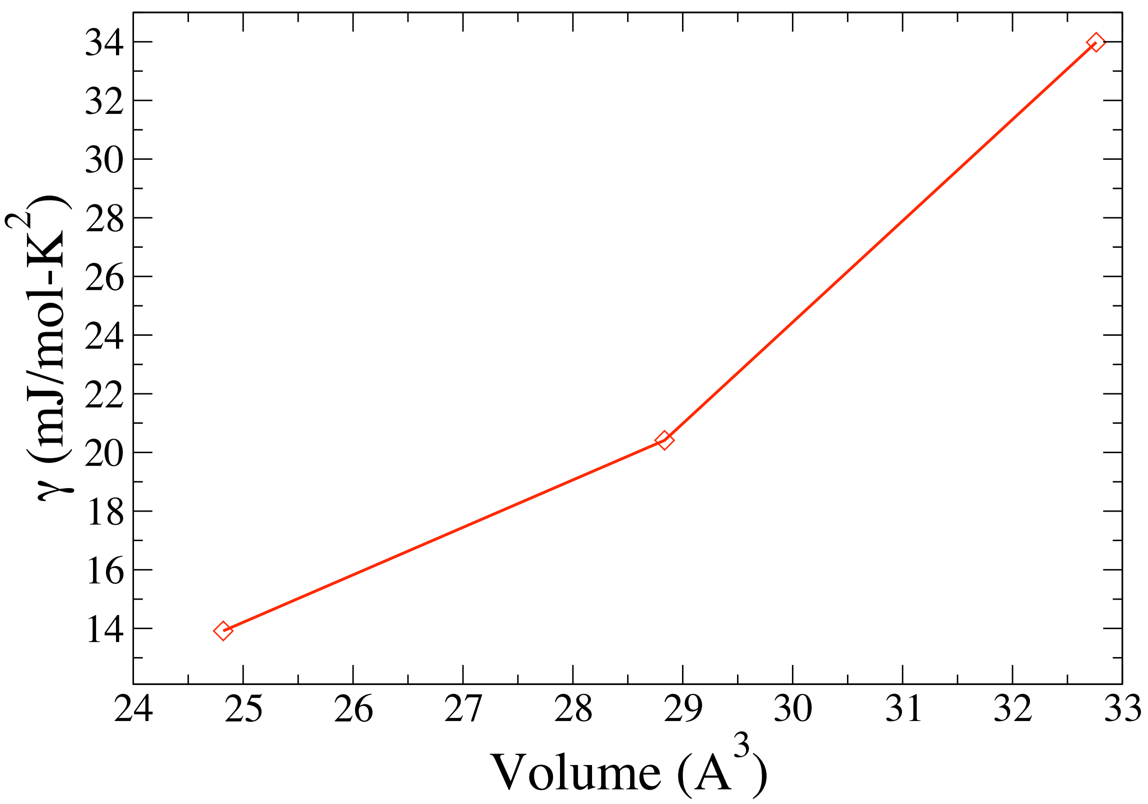
$\longrightarrow$ Huge expt. variation

- Cause of discrepancy:

$\longrightarrow$ Density self-consistency

$\longrightarrow$ number of f electrons

$\longrightarrow$ Inaccurate experiments?




$$\gamma = \frac{2\pi k_B^2}{3} \sum_\alpha \frac{\rho_\alpha(0)}{Z_\alpha}$$

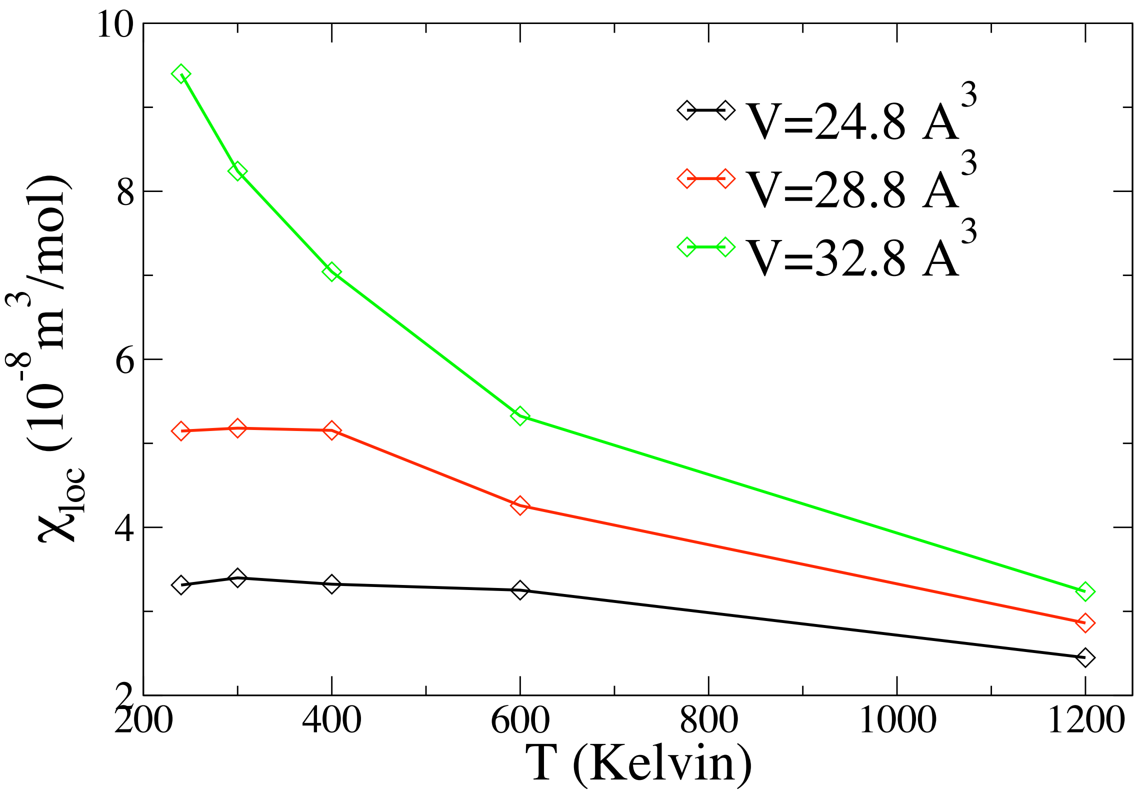
# Magnetic Susceptibility $\chi$

- First calculation of $\chi$ in Pu
- Pauli behavior $\Rightarrow$ itinerant electrons
- Curie behavior $\Rightarrow$ localized electrons
- Predict Pauli behavior for $V_{eq}$

$\longrightarrow$ Agrees with experiments

$\longrightarrow$ Explains lack of magnetism

- Expanded lattice agrees with $PuH_2$.




**We have observed quantum decoherence in Pu**

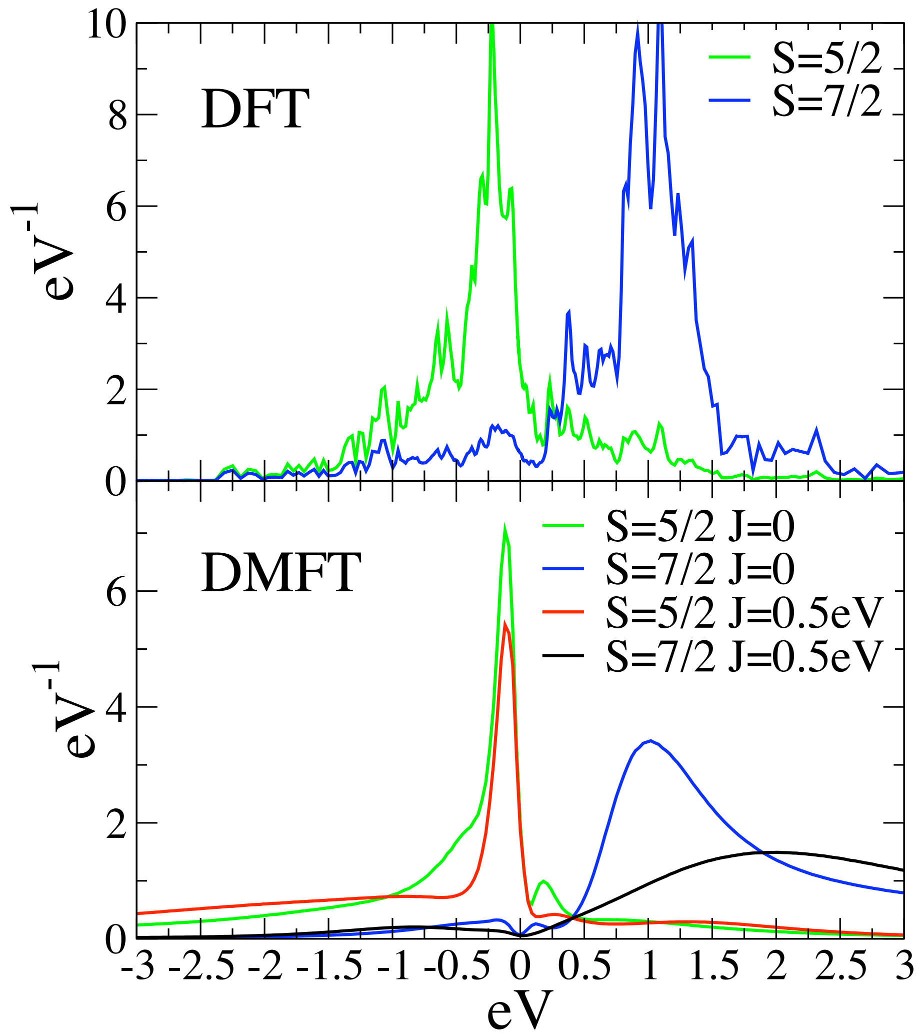
# Photoemission spectra

- Density of electronic states versus energy.

- DMFT renormalizes DFT spectrum

→ Transfer of weight from Fermi energy to Hubbard bands

- Exchange causes further renormalization of spectrum.




**Exchange has notable effect on spectra**

# Future Work

- Compute electronic properties of $\alpha$ Pu

$\longrightarrow$ 16 atoms per unit cell

- Compute total energy as a function of volume for $\delta$ Pu

$\longrightarrow$ Clearly elucidate volume collapse

- Compute negative thermal expansion
- Make corresponding predictions for Pu alloys.

$\longrightarrow$ Am, Ga, vacancies

$\longrightarrow$ Show why alloying equates to pressure

# Computational and Scientific Impact

- First approximation-free exact DMFT calculation of Pu

$\longrightarrow$ *Impossible* without the power of Atlas

- Pu is shown to be a strongly correlated Fermi liquid

$\longrightarrow$ The moments in Pu are screened

$\longrightarrow$ DFT+DMFT is a pivotal tool for understanding strong correlated systems

- The use of massive parallel computation is critical to understanding the elusive properties of Pu.

# Presentations / Publications

- Invited talk APS 2008 - UCRL-ABS-236899

$\longrightarrow$ *Dynamical mean-field theory calculations of materials properties using the continuous time quantum Monte-Carlo method*

- Invited talk Pu Futures 2008 - LLNL-ABS-401407

$\longrightarrow$ *Electronic coherence in $\delta$ Pu: A DMFT study*

- Contributed talk MRS 2008 - UCRL-ABS-236117

$\longrightarrow$ *Electronic properties of Pu via the dynamical-mean field theory*

- Contribute talk APS 2008 - UCRL-ABS-236889

$\longrightarrow$ *Effects of full Coulomb interactions on electronic structure of delta-Pu*

- Publication in preparation